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**Ultrafiltration membrane mfr. - by dissolving dichloro-diphenyl sulphone bisphenol condensed copolymer in mixed solvent, immersing in water and then methanol**

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Patent Family:

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Abstract (Basic): JP 56091815 A

Method comprises (a) dissolving dichlorodiphenylsulphone- bisphenol condensed copolymer into a mixed solvent consisting of solvent which is good solvent for the copolymer and miscible with water and solvent which is poor solvent or nonsolvent for the polymer and immiscible with water, (b) pouring the resulting soln., (c) immersing into water and (d) immersing into methanol. The process makes it possible to prepare membrane having uniform quality, since process does not include heat-drying for removing solvent. The membrane is used for concentration and rejection of high polymer and colloid suspending in water.

In an example, with 90 ml DMF there was mixed 10 ml of xylene, and 20 g of polysulphone resin was dissolved into the mixed soln. The soln. was poured over polyethylene nonwoven fabric so as to be about 200 micron thickness, immediately after, the casting was immersed into methyl alcohol maintained at 10 deg.C, and stood for 24 hr, and again immersed into water. The resulting membrane exhibited water transmissivity rate of 180 L/m<sup>2</sup>.hr under 0.5 kgG/cm<sup>2</sup>. The rejection of 0.2 wt.% aq. egg albumin soln. was 95%.

Derwent Class: A26; A32; A88; D15; J01

International Patent Class (Additional): B01D-031/00

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## SPECIFICATION

### 1. TITLE OF THE INVENTION

#### PROCESS FOR PRODUCING ULTRAFILTRATION MEMBRANE

### 2. CLAIMS

1. A process for producing an ultrafiltration membrane, comprising the steps of: dissolving a dichlorodiphenylsulfone/bisphenol copolycondensate resin in a mixed solvent of a solvent which is a good solvent for the resin and highly miscible with water and a solvent which is a good solvent or non-solvent for the resin and not miscible with water; casting the resin solution onto a porous support; and immersing the support in water and then in methanol.
2. The process for producing an ultrafiltration membrane according to claim 1, wherein the solvent highly miscible with water is N,N-dimethylformamide, N,N-dimethylacetamide or N-methyl-2-pyrrolidone.
3. The process for producing an ultrafiltration membrane according to claim 1 or 2, wherein the solvent not miscible with water is an aromatic hydrocarbon such as benzene, toluene or xylene, a halogenated hydrocarbon such as carbon tetrachloride or chloroform, or an aliphatic hydrocarbon such as n-hexane, n-heptane or octane.

### 3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process for producing an ultrafiltration membrane from dichlorodiphenylsulfone/bisphenol copolycondensate resin (hereinafter referred to as polysulfone resin).

The present invention is intended to produce, using polysulfone resin, an ultrafiltration membrane which has an asymmetric structure, whose dense surface layer (skin layer) has pores with a uniform pore size, and which excels in separation performance.

There has been performed a process for producing an asymmetric membrane, what is called wet membrane formation, in which a synthetic resin solution is cast onto a porous support, part of the solvent is vaporized, the resultant support is immersed in a solvent that is a non-solvent for the synthetic resin, but a good solvent for the solvent dissolving the synthetic resin to solidify the resin, so that an asymmetric membrane whose one face, where the solvent has been vaporized, is dense and opposite face is porous. In such a process, a mixed solvent of a volatile good solvent and a non-volatile good solvent is used as a solvent for the synthetic resin. The membrane thus obtained is used to separate or concentrate water-soluble polymers or colloids under pressure of 0.5 to 10 kg weight/cm<sup>2</sup>.

And there is proposed a process for producing an asymmetric ultrafiltration membrane using polysulfone resin as a raw material (U.S. Patent No. 3567810) in which, in accordance with the above described wet-phase separation membrane formation, the polysulfone resin is dissolved in a mixed system of two kinds of solvents (such as acetone and N-methyl-2-pyrrolidone), the polysulfone resin solution is cast onto a porous support, part of the solvent is vaporized at high temperatures, the support is immersed in a non-solvent such as water. However, such a process has disadvantages in that it is very difficult to accurately control the amount of the solvent vaporized in the operation of vaporizing the solvent at high temperatures, and thus, the separation performance of the resultant ultrafiltration membrane, that is, the reproducibility of the molecular weight cutoff or pure water permeation is poor.

After directing tremendous research effort toward the reproducibility, separation performance and water permeation performance of a polysulfone ultrafiltration membrane, the present inventors have found a process for producing a high-performance polysulfone resin ultrafiltration membrane, in which a small amount of hydrophobic organic solvent is added to the membrane forming solution where polysulfone resin is dissolved, thereby allowing a

high-temperature vaporization operation to be eliminated. And finally they have accomplished the present invention.

Specifically, the present invention is a process for producing a polysulfone ultrafiltration membrane, comprising the steps of: dissolving a polysulfone resin in a mixed solvent of a solvent which is a good solvent for the polysulfone resin and highly miscible with water and a solvent which is a good solvent or non-solvent for the polysulfone resin and not miscible with water to prepare a membrane forming solution; casting the membrane forming solution onto a porous support; immersing the support in water to solidify the polysulfone resin and fully wash the solidified resin; and immersing the washed membrane in methyl alcohol to extract the hydrophobic organic solvent remaining in the polysulfone resin.

Solvents applicable to the present invention which dissolve polysulfone resin and are highly miscible with water include: for example, N, N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone. As the other solvent which is not miscible with water, aromatic compounds such as benzene, toluene and xylene or aliphatic hydrocarbons such as n-hexane, n-heptane and octane whose boiling points are all 40°C or higher at atmospheric pressure are suitably used. Besides, halogenated hydrocarbons such as chloroform and carbon tetrachloride can also be used.

The mixing ratio of the hydrophobic solvent to the hydrophilic solvent that dissolves the polysulfone resin is 15% or less on the basis of volume fraction. By varying the mixing ratio, the cut-off performance (pore size) of the membrane can be varied while keeping the concentration of the polysulfone resin constant. It is not recommended to use the hydrophobic solvent at a mixing ratio higher than 15%, on the basis of volume fraction, because if the volume fraction is higher than 15%, aggregation may occur in the hydrophobic solvent when the support is immersed in water after the step of casting the membrane forming solution onto a porous support, thereby causing pin-hole like pores on the face of the membrane.

A membrane forming solution prepared by dissolving 10 to 55% by weight of polysulfone resin in a solvent system having the above described composition is cast onto the surface of a porous support, such as a polyethylene nonwoven fabric or polyethylene sintered plate, and the

resultant support is immersed in water. This operation allows the polysulfone resin to solidify, thereby forming a membrane on the porous support. The membrane is fully washed in water to wash the water-soluble solvent off almost completely and then immersed in methyl alcohol to extract the hydrophobic organic solvent which has not been extracted in water, but remains in the membrane.

Production of an ultrafiltration membrane by the process of the present invention is very effective from an industrial point of view, because it does not include a step of drying solvent with heat, thereby creating few production variations.

The ultrafiltration membrane produced by the process is not only effective in concentrating or eliminating polymers or colloids that are dissolved in water, but also useful in separating polymers having different molecular weights from each other.

In the following the above described points will be described by several examples.

#### Example 1

Ten ml of xylene was mixed with 90 ml of N,N-dimethylformamide, and 20 g of polysulfone resin was dissolved in the mixed solution to prepare a membrane forming solution. The membrane forming solution was cast onto a polyethylene nonwoven fabric to about 200  $\mu\text{m}$  thick and subsequently immersed in water at 3°C. After 5-hour immersion in water, the membrane was immersed in methyl alcohol at 10°C, allowed it to stand for 24 hours, and again immersed it in water to replace methyl alcohol with water.

The membrane exhibited a water permeation of 180 l/m<sup>2</sup>.hr under pressure of 0.5 kg weight/cm<sup>2</sup> and a rejection rate of 95% against 0.2% by weight of egg albumin solution. The rejection rate herein used is defined by the following equation.

$$\text{Rejection rate (R)} = 1 - (\text{Concentration of liquid permeate} / \text{Concentration of stock solution}) \times 100 \\ (\%)$$

### **Example 2**

85 ml of N-methyl-2-pyrrolidone was mixed with 15 ml of chloroform, and 35 g of polysulfone resin was dissolved in the above mixed solution to prepare a membrane forming solution. A membrane was obtained using the membrane forming solution through the same procedure as in Example 1. The membrane exhibited a pure water permeation of 80 l/m<sup>2</sup>.hr under pressure of 1.5 kg weight/cm<sup>2</sup> and rejection rates of 100%, 100% and 70% against solutions of 0.2% by weight of egg albumin, 0.1% by weight of myoglobin and 0.05% of vitamin B-12, respectively.

### **Example 3**

90 ml of N,N-dimethylacetamide was mixed with 10 ml of octane, and 15 g of polysulfone resin was dissolved in the above mixed solution to prepare a membrane forming solution. 14 membranes were obtained by using the membrane forming solution and repeating the same procedure as in Example 1 14 times. These membranes exhibited rejection rates of 78 to 87% against 0.1% by weight of bovine serum albumin solution, which confirmed good reproducibility of the membrane formation.

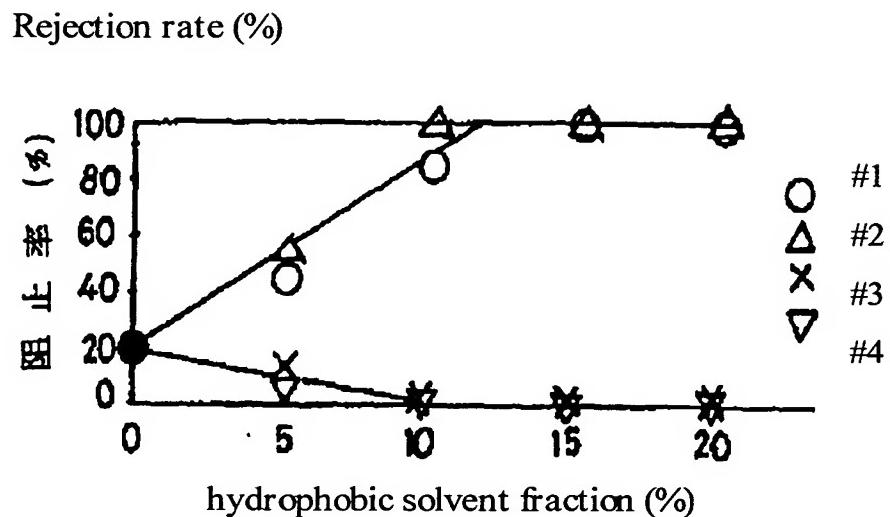
### **Example 4**

Membranes were formed through the same procedure as in Example 1 using N,N-dimethylformamide as a hydrophilic solvent, chloroform, carbon tetrachloride, toluene or xylene as a hydrophobic solvent, and 20% by weight of polysulfone resin. The influence of the mixing ratio of the solvents on the rejection rate against 0.1% by weight of myoglobin was observed. The results are shown in Figure 1. The figure shows that the membrane performance can be controlled by the combination and mixing ratio of solvents.

## **4. BRIEF DESCRIPTION OF DRAWING**

Figure 1 is a graph showing the relationship between the mixing ratio of solvents and the rejection rate against 0.1% myoglobin solution.

Figure 1



- #1 Chloroform
- #2 Carbon tetrachloride
- #3 Toluene
- #4 Xylene